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Research Note

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Dislocation Studies in Diamond by X- Ray Diffraction Microsco

F. EULER
G. H. SCHWUTTKE

FOR ERRATA

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THE FOLLOWING PAGES ARE CHANGES

TO BASIC DOCUMENT

AFCRL-63-65   March 1963

Dislocation Studies in Diamond by X-Ray
Diffraction Microscopy

F. Euler
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ERRATA

page 3, TABLE 1, last column:

Change from: to:

Shown in Figures		Shown in Figures
1		1
2		2
3 and 4		3,a and b
5		3,c
6		4,a
7 and 8		4,b and c

Page 4, Figure 1: The scale is approximately 7x (not 10x). The horizontal striations are artifacts produced by the lettering on the preceding page. The vertical striations represent impurity fluctuations in the sample.

Page 6, Figure 3: The scale is approximately 20x (not 25x).

Page 7, Figure 4: The scale is approximately 20x (not 25x).

Page 13, Figure 7: The authors apologize for the distracting ink spot in the top section.
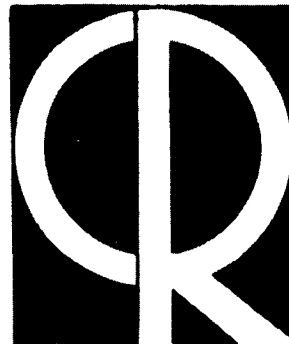
Research Note

Dislocation Studies in Diamond by X- Ray Diffraction Micro:

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Bayside, New York

Abstract

Diamonds of both type I and type IIb have been studied by X-ray diffraction microscopy. Long-range strain fields are the dominating imperfections in the former, and dislocations appear to be closely related to strain centers. The latter show a much higher density of edge dislocations with Burgers vectors in the (111) planes.

These studies corroborate the general view that type I diamond is more perfect but also more strained and type II close to mosaic and less strained. The new findings are discussed in comparison with the birefringence and X-ray diffraction phenomena observed in types I and II diamond.

Contents

Illustrations

Dislocation Studies in Diamond
by X-Ray Diffraction Microscopy

1. INTRODUCTION

The two types of diamond, I and II, as distinguished mainly by their optical properties,[1] show also other characteristic differences which are related to their structure. The following three phenomena have been observed in type I diamonds only:

1) X-ray asterism;[2] that is, the extension of the scattering regions at the reciprocal lattice points along the axes.

2) Presence of submicroscopic platelets[3] parallel to the cube planes, in sharply defined regions on electron transmission micrographs.

3) Presence of nitrogen,[4] up to 0. 2 atomic percent. Proportional to the N-concentration are the absorption coefficients at 7. 8 μ and 3065 Å and an increase of the lattice constant.

X-ray asterism, in general, points to the presence of strain. Its particular orientation suggests that this strain is caused by (100) planar crystal imperfections. These are the observed submicroscopic platelets, most likely nitrogen precipitations. An N-C-N layer[5] would account for the local displacement of lattice planes required for the intensity of the X-ray asterism on different Bragg reflections.[6]

It appears, then, that type I diamonds are characterized by the presence of strained regions in which nitrogen is precipitated.

On the other hand, it has been found that the Bragg reflections are 3 to 8 times stronger[7,8] in type II, due to lack of primary extinction, to the degree of an almost

mosaic crystal. Thus, the precipitate-infested type I seems to be more perfect than the precipitate-free type II. In order to resolve the apparent paradox, this study of dislocations has been undertaken.

During the last five years, dislocations in diamond have been postulated to account for the trigons[9] and slip lines[10] found on natural (111) faces. They also have been shown directly by X-ray topography.[11,12,13] Unfortunately, in these articles the type of samples was not specified. The work presented here aims to show characteristic differences between semiconducting and insulating diamonds. While the latter may represent type I with a 9:1 chance, the former belong to the very rare subtype IIb (1 in 50,000) of type II.[14] Whether they are representative of the whole type II is open to question.

2. EXPERIMENTS

For diffraction microscopy, X rays are transmitted through a wafer shaped crystal cut and oriented in such a way that a Bragg reflection is produced, which may be conveniently recorded on a film behind the sample. The X rays either may be parallel throughout the width of the sample or a narrow beam may scan sample and film. Contrast in the recorded image is due to one of two effects: primary extinction[11] or anomalous transmission.[15] The latter is described by the formation of standing waves between perfect reflecting lattice planes. The choice between these two effects is determined by the product of the linear absorption coefficient μ and the sample thickness t. Extinction contrast requires: $\mu . t \approx 1$, anomalous transmission: $\mu . t \approx 20$. Both methods may be used to reveal impurities, strain areas, and dislocations. In the work reported here, extinction contrast was used. Good resolution requires a rather perfect crystal. In the case of dislocations, the image constrast (see Appendix) is proportional to the scalar product of the Burgers vector and the diffraction vector normal to the reflecting planes. Therefore, if different sets of reflecting planes are used, the intensity of the imperfection image is usually different in.the case of dislocations. However, the intensity does not change with impurities.

3. RESULTS

X-ray diffraction micrographs were obtained from 11 semiconducting and 11 insulating diamonds. Only a limited selection is shown here. This, however, can be considered representative in regard to the features exhibited. Table 1 presents a list of the sample data.

TABLE 1.   Material, shape, and size of samples

No.	Material	Shape	Area (mm^2)	Thick-ness (mm)	Shown in figures
Si1	Silicon	Disk	300	1	1
Si2	Silicon	Wafer	200	1	2
	Diamond				
Sc1	Semiconducting	Plate	2	1.8	3 and 4
Sc2	Semiconducting	Plate	24	3	5
In1	Insulating, gem	Rectangular cut	10	Max. 2	6
In2	Insulating, gem	Rectangular cut	8	Max. 2	7 and 8

The silicon samples (Figures 1 and 2) are shown here merely to demonstrate the capability of the method and the degree of perfection possible in these laboratory-grown semiconductor crystals. Figure 1 shows a perfect crystal with no dislocations and no strain. Figure 2 reveals individual dislocations in some areas and a dense network of more than 10^6 dislocations/cm^2 in other parts of the crystal. In contrast to these photographs, the images obtained from the diamond samples are much less perfect for a number of reasons. First, unfavorable thickness of the samples for either method ($\mu.t\approx3$ for Mo $K\alpha$ radiation); second, prohibition of sample alteration; third, uncleaned sample surfaces; fourth, lack of crystal perfection as compared to silicon.

Figures 3a and 3b show the same semiconducting diamond. The diffraction images were obtained with the use of two different sets of reflecting lattice planes, (220) in Figure 3a and (111) in Figure 3b. Their different appearance demonstrates clearly that the crystal imperfections are dislocations. Since (111) produces a much lighter image, it is concluded that the Burgers vector of most dislocations lies in (111) planes, most likely due to slip. Such slip in octahedral planes is common to other substances with diamond lattices. The dislocations produced form an angle of 60° with their Burgers vectors (see Appendix). In Figures 3a and 3b, the dislocations occur in heavy, unresolved clusters (more than 10^6 dislocations/cm^2), which coincide with strain centers revealed by birefringence under polarized light. Figure 3c presents a second sample of semiconducting diamond, roughly to scale with the first one. Again, unresolved clusters appear in some areas, while in others individual dislocations are visible. The light area at one corner is misoriented by several minutes of arc.

Figure 4a shows the first of two selected samples of insulating diamond. It clearly exhibits a strain center (located near one of the long edges) from which numerous dislocations radiate, a pattern typical for most of our insulating samples.
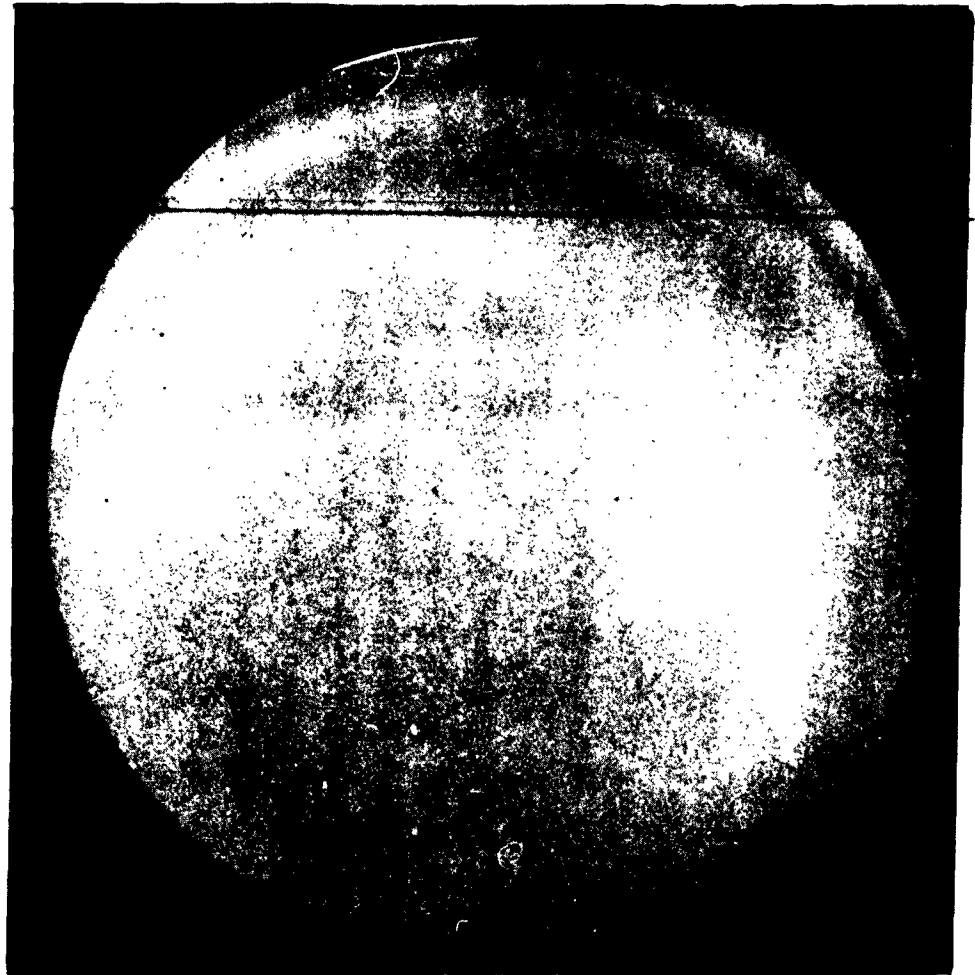
Figure 1. X-ray Diffraction Micrograph of Perfect Silicon Disk (approx. 10x)
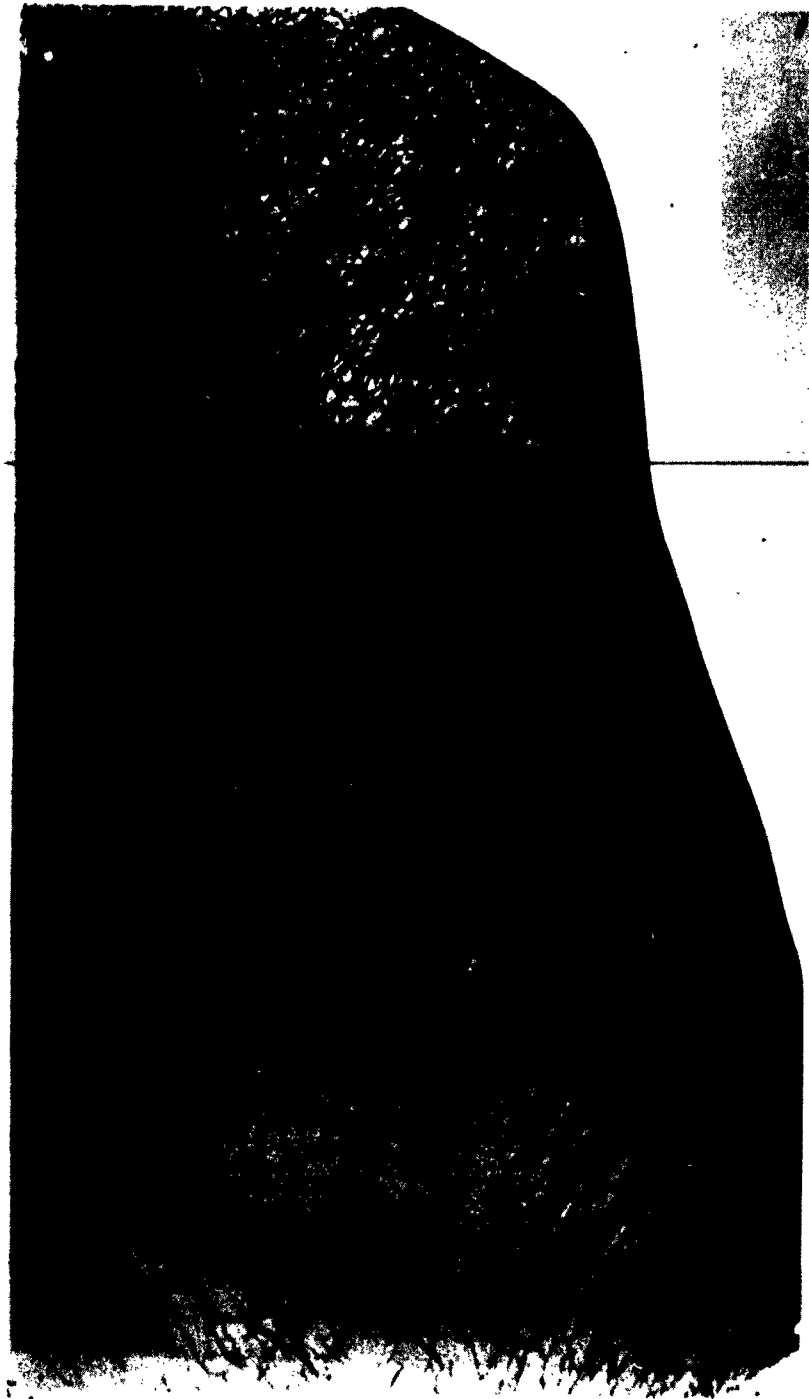
Figure 2. Dislocations in Silicon Wafer (approx. 10x)

Figure 3a.

Figure 3b.

Figure 3c.

Figure 3.   Dislocation Clusters in Semiconducting Diamond (approx 25x): (a) Sample Sc1 in 220 Reflection; (b) Sample Sc1 in 111 Reflection; Reduced Contrast Due to Situation of Burgers Vector in (111) Plane; (c) Sample Sc2 in 220 Reflection.

Figure 4a.
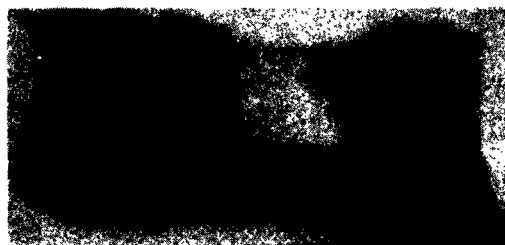
Figure 4b.

Figure 4c.

Figure 4. Dislocations in Insulating Diamond (approx. 25x): (a) Sample In1 in 220 Reflection, Dislocations Radiating from Strain Center; (b) Sample In2 in 220 Reflection. Dislocations appear broad due to superimposed long-range strain; (c) Sample In2 in 111 Reflection. Dislocations have disappeared due to situation of Burgers vectors in (111). Long-range strain causes uniform gray appearance.

Already, Lang[11] had shown a most beautiful example of nearly perfect diamond. He could resolve individual radiating dislocations. Some of the extreme black areas on Figure 4a disappeared when $\bar{2}20$ reflection was used (instead of 220); that is, the Burgers vector of these dislocations lies in the ($\bar{1}10$) plane.

Figures 4b and 4c show the second insulating diamond in (220) and (111) reflection. All dislocations shown on Figure 4b are not visible in Figure 4c as their Burgers vector lies in the reflecting (111) plane. The remaining gray appearance is attributed to uniform strain which is also responsible for the broadness of the dislocation images shown in Figure 4b.

4. DISCUSSION

In summary, all diamonds are rather imperfect compared to Ge or Si, showing dislocations and strain. The difference between semiconducting and insulating diamonds lies (1) in the distribution of dislocations and strain and (2) in the degree of perfection. In semiconducting diamonds, the distribution of dislocations and strain is such that high dislocation density coincides with high strain. In insulating diamonds, long-range strain fields dominate; dislocations radiate from strain centers.

These radiating dislocations were first postulated by F. C. Frank,[9] who observed that trigons on octahedral faces were located on top of strain centers in the interior. Whether the long-range strain fields coincide with the areas in which Evans and Phaal[3] observed the nitrogen platelets is still open to question. It also would be interesting to know whether there exists a connection between strain fields and cleaving. Raal[16] mentions that type II cleaves easier than type I, which is inclined to shatter with curved surfaces.

The coinciding areas of high dislocation density and high strain appear to be connected with the existence of slip planes. Tolansky[10] observed octahedral slip planes in 6 out of 100 samples. This frequency of occurrence may possibly indicate that slip planes are characteristic for type II. Note that the Burgers vectors observed in our semiconducting diamonds lie in octahedral planes.

With regard to perfection, semiconducting diamonds show dislocation clusters with densities high enough to identify the crystal as mosaic. Insulating diamonds are somewhat more perfect; that is, the dislocation density is, in general, substantially less.

Table 2 lists the reflection characteristics of diamonds as observed in types I and II or, in the case of dislocations, insulating and semiconducting diamond. If one could equate type I with insulating and type II with semiconducting diamond, high perfection would coexist with high N-concentration and low dislocation density

and vice versa. In other words, the dislocation density (and not the precipitate concentration) determines the difference in Bragg intensities. Furthermore, dislocation density and precipitate concentration are, in the case of diamonds, inverse characteristics. This is consistent with the hypothesis that the submicroscopic (100) platelets of precipitated nitrogen prevent the occurrence of slip in (111) planes in type I and subsequently the development of slip dislocations, which are so numerous in type II, where no nitrogen is precipitated.

TABLE 2. Perfection of diamonds

	Type I	Type II
Bragg intensities (perfection)	Weak (perfect)	Strong (mosaic)
N-precipitate concentration	Up to 0.2 atomic percent	None
	Insulating	Semiconducting
Dislocation density	Substantially less	More than $10^6/cm^2$

Table 3, which is self-explanatory, summarizes the conclusions. The symbols A and B conform to Raman's[18] nomenclature of diamond classification. Table 3 does not represent a complete listing of all the physical properties that are different in sets A and B, but only the most characteristic.

TABLE 3.   Classification of diamonds

Types
I. More than 9 in 10. Mixture of macro and microscopic regions with two sets of characteristics: A and B.

II. Set B characteristics only.
        Subtypes: IIa insulating   [14]   (less than 1 in 10)
                       IIb semiconducting   (1 in 50,000)

Sets of characteristics

A.   Crystal regions contain up to 0.2 atomic percent nitrogen[4]

      precipitated in submicroscopic {100} platelets,[3]

      are strained [X-ray asterism along <100> directions,[2,6]

                long-range strain patterns by

                      birefringence[9] and

                      X-ray topography[11]] ,

    but rather perfect

               [strong primary extinction of X rays[7,8]] .

Properties proportional to N-concentration:[4]
    increase in lattice constant,
    absorption coefficients at 7.8 μ and 3065 Å.

B.   Crystal regions contain no precipitates, show no absorption

    at 7.8 μ,[1] have uv edge at 2250 Å.

Strain confined to {111} slip planes

                [lamellar birefringence,[17,18]

                trigon rows define slip planes[10]] .

Dislocations: in {111} planes

              clusters of more than $10^6/cm^2$,

              submicroscopic <112> dipoles,[3]

              60° Burgers vector in {111} planes.

Weak primary extinction of X rays as in mosaic crystals

          [Bragg intensities 3 to 8 times stronger[8]

          than in type I (average A and B)] .

5. PRESENTATIONS

A resume of this work was presented at the 20th Pittsburgh Diffraction Conference[19] while, earlier, the experimental results were used in a presentation of the First International Congress on Diamonds in Industry.[20]

Readers who wish a more comprehensive and detailed review of the physical properties of diamond are referred to a recent publication by A. D. Johnson.[21]

Appendix

X-RAY DIFFRACTION AND BURGERS VECTOR OF A DISLOCATION

The relationship between the Burgers vector and a diffracting lattice plane may easily be visualized in Figure 5, which shows an edge dislocation[22] and its corresponding Burgers circuit and vector. Reflecting lattice planes chosen so that they include the Burgers vector are almost undisturbed by the dislocation; primary extinction and anomalous transmission are that of a perfect crystal. In contrast, lattice planes perpendicular to the Burgers vector are severely disturbed at the dislocation. Local change in lattice plane spacing destroys the Bragg condition for the incident beam and interrupts its diffraction. Consequently, lack of both primary extinction and anomalous transmission produces image contrast. The same relationships hold for screw dislocations, as shown in Figure 6.

The situation of slip in the diamond lattice is illustrated in Figure 7 which shows the arrangement of atoms in {100}, {110}, and {111} projection planes. The latter exist as double layers which may slip in the directions <110> as indicated and produce dislocations extending along the <110> axis a which includes an angle of 60° with the Burgers vector b.

12
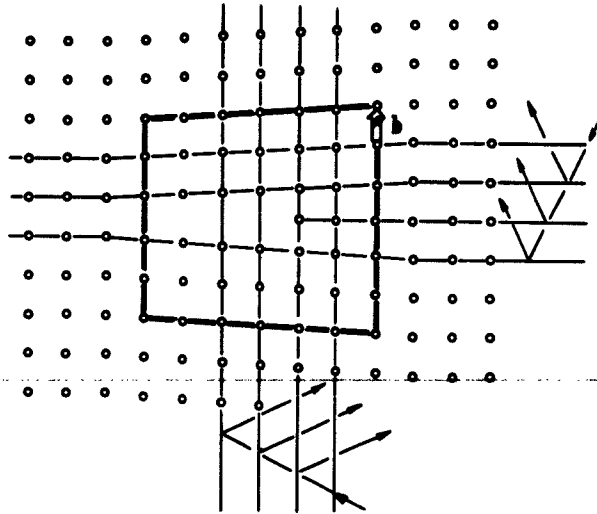
Figure 5. Burgers Circuit and Vector b of Edge Dislocation. Lattice planes containing b experience very little disturbance. Those perpendicular to b vary drastically in spacing at the dislocation.
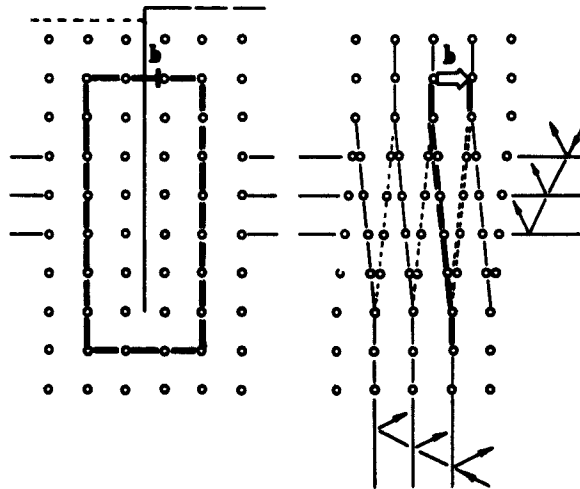
Figure 6. Burgers Circuit and Vector b of Screw Dislocation. a) Top view: all lattice planes contain b, almost no disturbance. b) Side view: lattice planes perpendicular to b are interrupted at the slip plane. More contrast across than in slip plane.
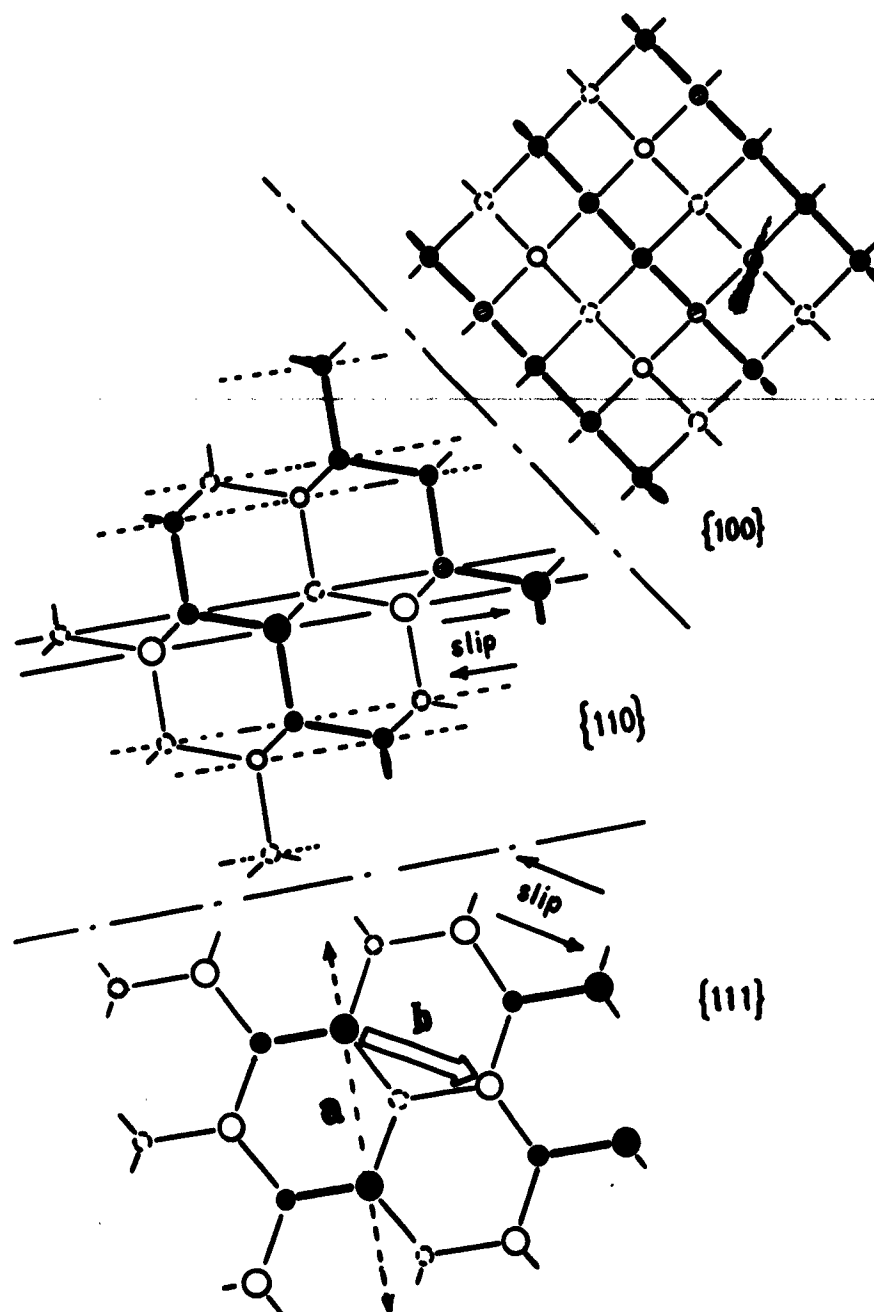
Figure 7. Diamond Lattice. Arrangement of atoms in cube {100}, dodecahedral {110} and octahedral {111} planes of projection. The last form double layers which may slip and produce dislocations extending along the axis (a) which includes an angle of 60° with the Burgers vector b.

References

1. R. Robertson, J. J. Fox, and A. E. Martin, Philos. Trans. A232, 463 (1934).

2. K. Lonsdale, Proc. Phys. Soc. (London) 84, 314 (1942).

3. T. Evans and C. Phaal, Paper B4 of 5th International Cong. of Electron Micro-scopy, Academic Press, Inc., New York, 1962.

4. W. Kaiser and W. L. Bond, Phys. Rev. 115, 857 (1959).

5. R. J. Elliott, Proc. Phys. Soc. 76, 787 (1960).

6. J. A. Hoerni and W. A. Wooster, Acta Cryst. 8, 187 (1955).

7. K. Lonsdale, Philos. Trans. A240, 219 (1947).

8. M. Renninger, Acta Cryst. 8, 606 (1955).

9. F. C. Frank, K. E. Puttick, and E. M. Wilks, Phil. Mag. 3, 1262 (1958).

10. S. Tolansky, A. Halperin, and S. H. Emara, Phil. Mag. 3, 675 (1958).

11. A. R. Lang, J. Appl. Phys. 30, 1748 (1959).

12. F. C. Frank and A. R. Lang, Phil. Mag. 4, 383 (1960).

13. A. Guinier and E. Guyon, J. Appl. Phys. 30, 622 (1959).

14. J. F. H. Custers, Physica 18, 489 (1952); 20, 183 (1954).

15. G. H. Schwuttke, J. Appl. Phys. 33, 2760 (1962).

16. F. A. Raal, Proc. Phys. Soc. 74, 647 (1959).

17. G. N. Ramachandran, Proc. Indian Acad. Sci. A24, 65 (1946).

18. C. V. Raman, Proc. Indian Acad. Sci. 55, 1 (1962).

19. F. Euler and G. H. Schwuttke, 20th Pittsburgh Diffraction Conference, Pittsburgh, Penn., 7-9 November 1962, Paper No. 16.

20. E. R. Czerlinsky, A. D. Johnson, and G. H. Schwuttke, First International Congress on Diamond in Industry, Paris, France, 31 May – 3 June 1962.

21. A. D. Johnson, "Diamond as a Semiconductor Material", Unclassified Report, AFCRL-62-535, July, 1962.

22. W. T. Read, Dislocations in Crystals, McGraw-Hill Book Co., New York, 1953, p. 14.

Card (top-right quadrant)

1. Diamonds
2. Semiconductors, crystal structure
3. Microscopy, X-ray diffraction

I. Euler, F. K.
II. Schwuttke, G. H.

AF Cambridge Research Laboratories, Bedford, Mass. Electronics Research Directorate
DISLOCATION STUDIES IN DIAMOND BY X-RAY DIFFRACTION MICROSCOPY by
F. K. Euler and G. H. Schwuttke. 17 pp. incl. illus.
January 1963
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